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Aluminium as anode in primary alkaline batteries. Influence of additives on the corrosion and anodic behaviour of 2S aluminium in alkaline citrate solution

K. B. SARANGAPANI, V. BALARAMACHANDRAN, V. KAPALI,
S. VENKATAKRISHNA IYER, M. G. POTDAR, K. S. RAJAGOPALAN

Central Electrochemical Research Institute, Karaikudi – 623 006, India

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The inhibitive effects of various additives on the corrosion of 2S aluminium in 4N NaOH containing calcium oxide and sodium citrate (base electrolyte) have been examined by studying the self corrosion, anodic polarization and anode efficiency of 2S aluminium in solutions containing different additives. It has been found that among the different additives investigated, those forming anions in solution act favourably.

1. Introduction

It has been reported that a combination of calcium ions and complexing agents such as citrate and tartrate can appreciably reduce the self corrosion of 2S aluminium in 1N NaOH solution and can also improve its efficiency for possible use as a galvanic anode [1–4]. These studies have led to the development of the primary battery system Al–alkaline citrate–MnO_2 [5]. Recent studies have shown that an alkali concentration as high as 4N NaOH can be chosen as the battery electrolyte by incorporating calcium hydroxide and sodium citrate in the right proportion so as to reduce the self corrosion by about 90% [6]. In the present study, the effect of a few additives on the corrosion, anodic polarization and anode efficiency has been examined.

2. Experimental details

2.1. *Metal specimens*

The specimens used for self corrosion studies were rectangular strips of 2S aluminium of not less than 99% purity and of size 5 x 2 x 0.2 cm^3. For anodic polarization and potential measurements, cylindrical rod specimens of 2S aluminium of uniform diameter (0.6 cm) and cross sectional area (0.8 cm^2) were used after embedding them in Teflon rods. A copper rod of diameter 0.6 cm was inserted into the other end of the Teflon to make a permanent contact with the embedded aluminium and this served as the electrical contact of the anode.

2.2. *Chemicals*

Sodium hydroxide, sodium citrate and all additives used were of LR (BDH) grade except for the rare earth elements. The additives were used as their oxides. The rare earth elements were procured from Indian Rare Earth Ltd, Alwaye. The calcium oxide was of high purity (BDH). It was ignited for a long time to decompose any calcium carbonate contained in the sample, cooled and stored in a dessicator before use. All solutions were prepared using distilled water.

3. Procedure

3.1. *Determination of inhibition efficiency*

Inhibition efficiency was determined by weight loss measurements. Triplicate specimens, polished with pumice powder and degreased in trichloroethylene were weighed and kept completely immersed in 300 ml of the test solution contained

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in a 400 ml beaker for 1 h. At the end of this period, specimens were taken out, washed well with running water, rinsed in distilled water, dried thoroughly and finally weighed. From the weight losses of specimens in alkali with and without added constituents the inhibition efficiency was calculated.

3.2. *Measurement of open circuit potential*

The open circuit potential of aluminium in different solutions was measured by keeping it in the solution for half an hour, during which time the potential became steady. The potential was measured using a Hg/HgO reference electrode, by means of a Zenith Digital Multimeter (Model ZE 1501).

3.3. *Polarization measurements*

Anodic and cathodic polarization of 2S aluminium in different solutions were carried out by drawing current from an indigenously fabricated current regulator. The working electrode consisted of a polished and degreased aluminium specimen and the auxiliary electrode was a platinum strip of area 4 cm^2. These were immersed in 200 ml of test solution kept in a 250 ml beaker, which was agitated by a magnetic stirrer. Polarization experiments were started after 30 min of immersion, when a steady potential was established. Current densities in the range 0.03–200 mA cm^{-2} were applied and potentials were measured after 5 min with reference to the Hg/HgO electrode. Each experiment was carried out in duplicate and average values of potential were taken for plotting the potential vs log current density curve.

3.4. *Anode efficiency determination*

This was determined by impressing various current densities within the range 50–150 mA cm^{-2}, using a platinum auxiliary electrode for a period of two hours. The working electrode and auxiliary electrode were kept immersed in 250 ml of the test solution which was agitated by means of a magnetic stirrer throughout the experiment. At the end of the experiment the specimen was removed and the weight loss determined. The anode efficiency was calculated using the relation

$$\text{anode efficiency (\%)} = \frac{\text{theoretical weight loss corresponding to the impressed current}}{\text{observed weight loss}} \times 100$$

4. Results and discussions

4.1. *Corrosion inhibition*

For the sake of convenience in discussing the experimental results, the additives used in this study can be grouped as follows:

i. cations (added as oxides)
ii. oxides giving rise to anions
iii. rare earths as oxides
iv. combinations of additives

Table 1 illustrates the influence of different cations in suppressing the self corrosion of 2S aluminum in 4N NaOH in the presence of calcium oxide and sodium citrate. It can be clearly seen from this table that all the cations under study have a very small influence on the inhibition efficiency as compared to the base electrolyte.

Table 2 gives the inhibition efficiency values obtained using amphoteric oxides which form anions in sodium hydroxide solution. It is interesting to note that several of these are effective in improving the inhibition efficiency obtained in the presence of calcium oxide and sodium citrate alone. The order of inhibition is as follows:

Table 1. Influence of additives (cation) on the corrosion of 2S aluminium in 4N NaOH

Serial no.	*Additives (cations) added to the base electrolyte*	*Inhibition efficiency (%)*
1	Base electrolyte alone	88
2	Base electrolyte + lithium	86
3	Base electrolyte + barium	81
4	Base electrolyte + strontium	83
5	Base electrolyte + magnesium	86
6	Base electrolyte + iron	79

Composition of base electrolyte: 4N NaOH containing 0.4% CaO and 20% sodium citrate; concentration of additive: 0.05%; duration of experiment: 1 h.

Table 2. Influence of additives (which give rise to anions in solution) on the corrosion of 2S aluminium in 4N NaOH

Serial no.	*Additives (which form anions) added*	*Inhibition efficiency (%)*
1	Base electrolyte alone	88
2	Base electrolyte + zinc	93
3	Base electrolyte + aluminium	93
4	Base electrolyte + arsenic	90
5	Base electrolyte + boron	87
6	Base electrolyte + bismuth	85
7	Base electrolyte + tin	84
8	Base electrolyte + antimony	83
9	Base electrolyte + lead	83
10	Base electrolyte + zirconium	81
11	Base electrolyte + vanadium	89
12	Base electrolyte + tellurium	87
13	Base electrolyte + tungsten	89
14	Base electrolyte + selenium	85

Composition of base electrolyte: 4N NaOH containing 0.4% CaO and 20% sodium citrate; duration of test: 1 h; concentration of additive added: 0.05%.

$$\mathrm{Zn}(93\%) \geqslant \mathrm{Al}(93\%) > \mathrm{As}(90\%) > \mathrm{B}(87\%) >$$

$$\mathrm{Bi}(85\%) > \mathrm{Sn}(85\%) > \mathrm{Sb}(84\%) > \mathrm{Pb}(83\%) > \mathrm{Zr}(81\%)$$

Table 3 gives the inhibition efficiency values obtained in the presence of rare earths as additives. All the rare earths behave almost identically and the results are similar to those obtained with cations, which show little influence on corrosion inhibition.

Table 4 brings out the influence of some of the combinations of additives on corrosion inhibition. The inhibition efficiency values are almost the same as in the case of individual additives forming anions.

Table 3. Influence of additives (rare earth elements) on the corrosion of 2S aluminium in 4N NaOH

Serial no.	*Additives (rare earth elements) added to the base electrolyte*	*Inhibition efficiency (%)*
1	Base electrolyte alone	88
2	Base electrolyte + terbium	83
3	Base electrolyte + praseodymium	82
4	Base electrolyte + neodymium	85
5	Base electrolyte + gadolinium	84
6	Base electrolyte + dysprosium	85
7	Base electrolyte + yttrium	87
8	Base electrolyte + cerium	84
9	Base electrolyte + lanthanum	87

Composition of electrolyte: 4N NaOH containing 0.4% CaO and 20% sodium citrate; duration of experiment: 1 h; concentration of additive added: 0.05%.

Table 4. Influence of combinations of additivies on the corrosion of 2S aluminium in 4N NaOH

Serial no.	*Combination of additives added*	*Inhibition efficiency (%)*
1	Base electrolyte alone	88
2	Base electrolyte + Sn (0.05%) + As (0.025%)	90
3	Base electrolyte + Zn (0.05%) + As (0.025%	90
4	Base electrolyte + Sn (0.05%) + Zn (0.05%) + As (0.025%)	92
5	Base electrolyte + Sn (0.05%) + As (0.01%)	92

Composition of base electrolyte: 4N NaOH containing 0.4% CaO and 20% sodium citrate; concentration of additive: 0.05%; duration of experiment: 1 h.

4.2. *Open circuit potential measurements*

Table 5 gives open circuit potential values for 2S aluminium in the base electrolyte containing various additives whose inhibition efficiencies are more than the base electrolyte. It is seen from the table that zinc, arsenic, vanadium, tungsten and selenium shift the potential of 2S aluminium to more negative values, whereas all the other additives shift the potential to more positive values. It is to be noted that the base electrolyte containing zinc, vanadium, tungsten and arsenic give higher values of inhibition efficiency also.

Incorporation of a combination of two or more additives is found to shift the potential to more negative values, and this combination of additives is also found to influence the inhibition efficiency favourably. Thus, additives which shift the potential in the negative direction, either alone or in combination with other suitable additives, may lead to the formulation of a base electrolyte to be used in batteries if incorporated in the base electrolyte.

4.3. *Anodic and cathodic polarization*

Fig.1 shows the anodic and cathodic polarization

Table 5. Open circuit potential of 2S aluminium in 4N NaOH solution containing CaO and sodium citrate in the presence of various additives

Serial no.	*Additives added*	*OCP of 2S aluminium in V with reference to Hg/HgO electrode*
1	Base electrolyte alone	— 1.36
2	Base electrolyte + zinc	— 1.446
3	Base electrolyte + arsenic	— 1.448
4	Base electrolyte + vanadium	— 1.372
5	Base electrolyte + tungsten	— 1.393
6	Base electrolyte + aluminium	— 1.33
7	Base electrolyte + selenium	— 1.468
8	Base electrolyte + 0.05% Zn + 0.025% As	— 1.454
9	Base electrolyte + 0.025% As + 0.05% Sn	— 1.458
10	Base electrolyte + 0.025% As + 0.05% Sn + 0.05% Zn	— 1.454
11	Base electrolyte + 0.05% Sn + 0.05% Zn	— 1.445

Composition of electrolyte: 4N NaOH containing 0.4% CaO and 20% sodium citrate; concentration of additive: 0.05%.

of 2S aluminium in the base electrolyte alone and in the presence of additives such as zinc and aluminium. As in the case of base electrolyte alone [6], the anodic polarization is found to be more than the cathodic polarization in the presence of these additives also, thereby clearly revealing the fact that the corrosion of 2S aluminium in the base electrolyte containing these additives is also

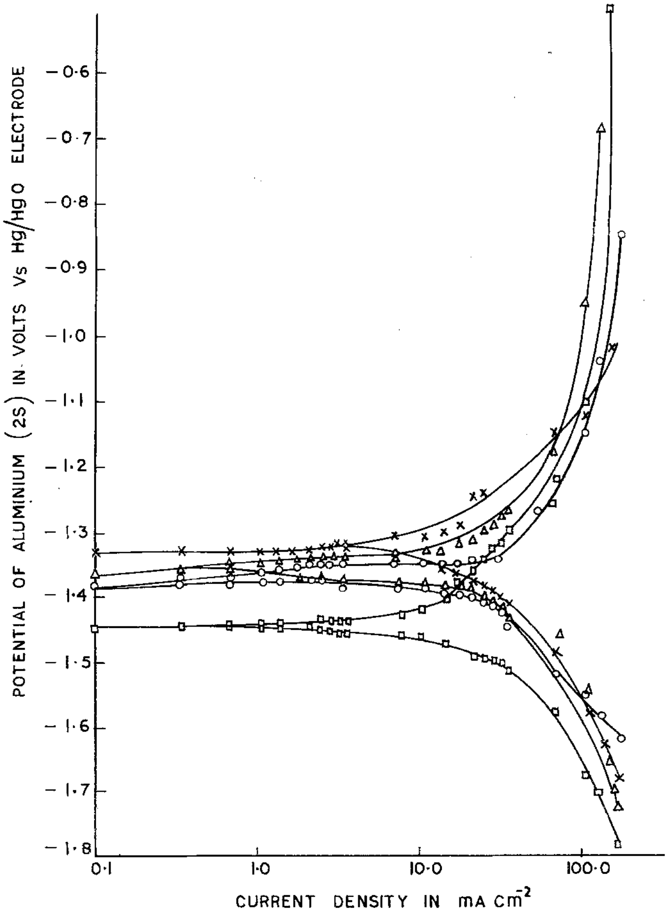

Fig. 1 Galvanostatic polarization of 2S aluminium in different solutions. o—o 4N NaOH alone; △—△ 4N NaOH containing 0.4% CaO + 20% sodium citrate; X—X 4N NaOH containing 0.4% CaO + 20% sodium citrate + 0.05% aluminium; □—□ 4N NaOH containing 0.4% CaO + 20% sodium citrate + 0.05% zinc.

under anodic control. This is also the case with other additives. A similar observation has been reported earlier [7], for the corrosion of aluminium in a potassium hydroxide solution containing calcium and calcium-containing organic compounds. It is possible that calcium and citrate have a synergistic inhibition effect on the corrosion of 2S aluminium in 4N NaOH solution. It is believed that the synergistic action of calcium and citrate may be due to the formation of a complex between calcium and citrate. The complex compound might be physically adsorbed, with calcium ions disposed towards the metal surface. Chemisorption of a calcium citrate complex has been ruled out on the basis of results obtained in radio tracer studies [6] using a Ca^{45}–Na citrate complex in the place of a non-radioactive Ca–Na citrate complex. With a concentration of 5% sodium citrate, the discrete complexes may tend to become attached to form bigger ligands, enhancing the coverage of the metal surface by these ligands. The possibility of formation of metal chelates in solutions of high alkalinity containing additional hydroxy ligands has already been reported [8]. The enhanced inhibition in the presence of additives such as zinc and aluminium can be attributed to the formation of complexes of citrate with these additives also, in addition to that with calcium.

Table 6 gives the extent of anodic polarization of 2S aluminium in the base electrolyte containing additives which form anions, for two different current densities. The polarization characteristics of 2S aluminium in the base electrolyte containing additives such as cations and rare earth elements are not included in this table, since they do not show any beneficial influence on inhibition efficiency and values of open circuit potential. From this table it can be clearly seen that minimum anodic polarization is produced by the addition of aluminium followed by tungsten, vanadium, selenium, arsenic and zinc. Incorporation of aluminium also enhances the inhibition efficiency to a higher value namely 93%, thereby favouring its addition in the base electrolyte to achieve a better battery electrolyte.

4.4. *Anode efficiency*

Table 7 gives the values of anode efficiency for 2S aluminum in the base electrolyte containing various additives forming anions in the solution, for various current densities. As the values of anode efficiency at low current densities of 10 mA cm^{-2} and 25 mA cm^{-2} were very low, they are not given in the table. At lower current densities, the wastage of aluminium is caused by the local cell action and also by the difference effect. It is seen from the table that the anode efficiency increases with the current density. At a current density of 150 mA cm^{-2} the anode efficiency of 2S aluminium in different electrolytes follows the order given below:

> Base electrolyte containing zinc (97%) > Base electrolyte (96%) > Base electrolyte containing arsenic, aluminium, tungsten and vanadium (all approximately 90%).

So the incorporation of zinc to the base electrolyte influences favourably the anode efficiency, and also the inhibition efficiency. Thus, its addition

Table 6. Anodic polarization characteristics of 2S aluminium in base electrolyte containing different additives

Serial no.	*Electrolytes used*	*Potential OCP (V)*	*With reference to Hg/HgO electrode*	
			110 mA cm^{-2}	*150 mA cm^{-2}*
1	Base electrolyte alone	−1.360	−0.95	−0.68
2	Base electrolyte + zinc (0.05%)	−1.446	−1.10	−0.34
3	Base electrolyte + arsenic (0.025%)	−1.448	−1.01	−0.85
4	Base electrolyte + vanadium (0.05%)	−1.372	−1.04	−0.89
5	Base electrolyte + tungsten (0.05%)	−1.393	−1.14	−0.97
6	Base electrolyte + selenium (0.05%)	−1.468	−1.16	−0.92
7	Base electrolyte + aluminium (0.05%)	−1.330	−1.12	−1.02

Table 7. Anode efficiency at various current densities for 2S aluminium in base electrolyte containing different additives

Serial no.	*Electrolyte used*	*Anode efficiency at various current densities (%)*				
		50 (mA cm^{-2})	*75 (mA cm^{-2})*	*100 (mA cm^{-2})*	*125 (mA cm^{-2})*	*150 (mA cm^{-2})*
1	Base electrolyte alone	51	75	90	90	96
2	Base electrolyte + zinc (0.05%)	52	65	88	89	97
3	Base electrolyte + aluminium (0.05%)	52	66	80	82	89
4	Base electrolyte + arsenic (0.05%)	56	72	84	85	89
5	Base electrolyte + tungsten (0.05%)	51	74	84	86	90
6	Base electrolyte + vanadium (0.05%)	52	73	84	86	91
7	Base electrolyte + selenium (0.05%)	52	54	78	80	84

Area of the aluminium (2S) electrode exposed: 10 cm^2; duration of experiment: 2 h.

to the base electrolyte to obtain the best battery electrolyte is positively indicated.

The choice of the best battery electrolyte, for a battery using aluminium as galvanic anode should satisfy the following requirements:

i. it should give maximum open circuit potential and minimum self corrosion
ii. it should give appreciable anode efficiency
iii. it should produce minimum anodic polarization and
iv. it should be of comparatively low cost.

Among the additives forming anions reported in this study, vanadium, selenium and tungsten do not show any marked influence on the inhibition efficiency nor on the anode efficiency. However, all of them have a favourable influence in shifting the open circuit potential to more negative values and in giving rise to minimum anodic polarization. Amongst all the additives studied, incorporation of aluminium into the base electrolyte brings about minimum anodic polarization even at very high current densities and also markedly enhances the inhibition efficiency. However its addition has no beneficial influence on the anode efficiency and the open circuit potential is shifted to a less negative value. Addition of zinc to the base electrolyte enhances the inhibition efficiency and also shifts the open circuit potential to a more negative value. But the anodic polarization, although low at low current density, becomes much higher at high current density. Moreover, the anode efficiency also is not improved by the presence of zinc.

5. Conclusion

On the basis of the foregoing discussion, it can be concluded that the incorporation of an appropriate combination of additives such as aluminium and zinc into the base electrolyte provides the formulation of a suitable battery electrolyte for use with 2S aluminium as the galvanic anode.

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